2. BASIS FOR EXPERIMENTAL DESIGN

This section provides a summary of knowledge about emissions, transport, and transformation of air pollutants in southern California, and integrates this knowledge into a "conceptual model" of the phenomena that should be reproduced by the regulatory ozone models. This section also describes the data requirements for data analysis and modeling. Together they form the basis for the experimental design of the SCOS97-NARSTO field measurement program.

There are five air basins in the SCOS97 domain (shown in Figure 2-1): the San Joaquin Valley (southern part of Kern County only), South Central Coast (Ventura County, Santa Barbara County and southern portion of San Luis Obispo County), South Coast, San Diego and Southeast Desert Air Basins (abbreviated SJVAB, SCCAB, SoCAB, SDAB, and SEDAB, respectively). The study area includes about 53,000 square miles in the southern portion of the State, with a population of more than 18 million. Seven percent of the entire U.S. population, and more than half the population of California, lives in the South Coast Air Basin alone. This region of California is an area of complex terrain (see Figure 2-2) — bounded by the Pacific Ocean to the west; to the north by narrow coastal mountains and valleys, the San Joaquin Valley, and the Sierra Nevada Mountains; and to the south and east by the California state border. Although the air basin boundaries were established with topographical features in mind, winds can and do transport pollutants from one basin to another.

2.1 Emissions

Section 39607(b) of the California Health and Safety Code requires the California Air Resources Board (ARB) to inventory sources of air pollution within the 14 air basins of the state and to determine the kinds and quantities of pollutants that come from those sources. The pollutants inventoried are total organic gases (TOG), reactive organic gases (ROG), carbon monoxide (CO), oxides of nitrogen (NO_X), oxides of sulfur (SO_X), and particulate matter with an aerodynamic diameter of 10 micrometers or smaller (PM_{10}). TOG consist of hydrocarbons including methane, aldehydes, ketones, organic acids, alcohol, esters, ethers, and other compounds containing hydrogen and carbon in combination with one or more other elements. ROG include all organic gases except methane and a number of organic compounds such as low molecular weight halogenated compounds that have been identified by the U.S. Environmental Protection Agency (EPA) as essentially non-reactive. For ROG and PM_{10}, the emission estimates are calculated from TOG and PM, respectively, using reactive organic fractions and particle size fractions. Emission sources are categorized as on-road mobile sources, nonroad mobile sources, stationary point sources, stationary area sources, and biogenic sources.

Major inventory efforts were undertaken by the ARB for several base years: 1987, 1989, 1990, 1991, and 1993 (California Air Resources Board, 1990a, 1991a, 1993a, 1994). Because the emission reductions that are required to show "reasonable further progress" are referenced in the 1990 Federal Clean Air Act Amendments to a 1990 base year, additional efforts were made in compiling the emissions inventory for that year. Table 2-1 shows the total TOG, ROG, CO and NO_X emissions in 1990, by county, for the SCOS97 study area. Tables 2-2 and 2-3 show the 1990 daily average by air basins for ROG and NO_X emissions, respectively. Emissions

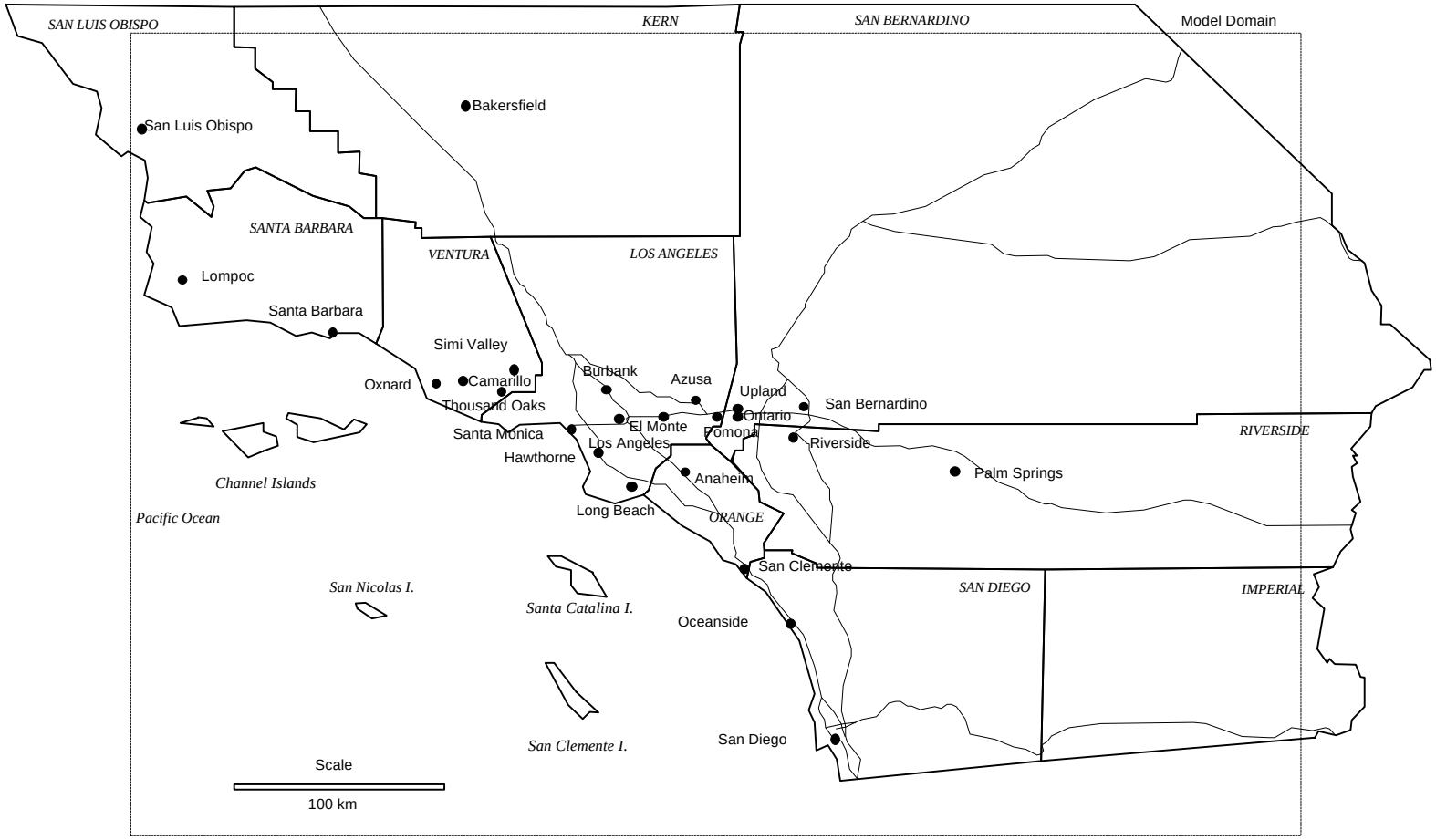
SAN LUIS OBISPO
KERN
SAN BERNARDINO
Model Domain
Bakersfield
San Luis Obispo
SANTA BARBARA
VENTURA
LOS ANGELES
Lompoc
Santa Barbara
Simi Valley
Oxnard
Camarillo
Thousand Oaks
Burbank
Azusa
Upland
San Bernardino
Ontario
Pomona
El Monte
Santa Monica
Los Angeles
Hawthorne
Riverside
RIVERSIDE
Palm Springs
Anaheim
Long Beach
ORANGE
Channel Islands
Pacific Ocean
San Clemente
San Nicolas I.
Santa Catalina I.
SAN DIEGO
IMPERIAL
Oceanside
San Clemente I.
San Diego
Scale
100 km

Figure 2-1. The SCOS97-NARSTO study area. Major cities, county boundaries, interstate highways, and the proposed modeling domain are shown.

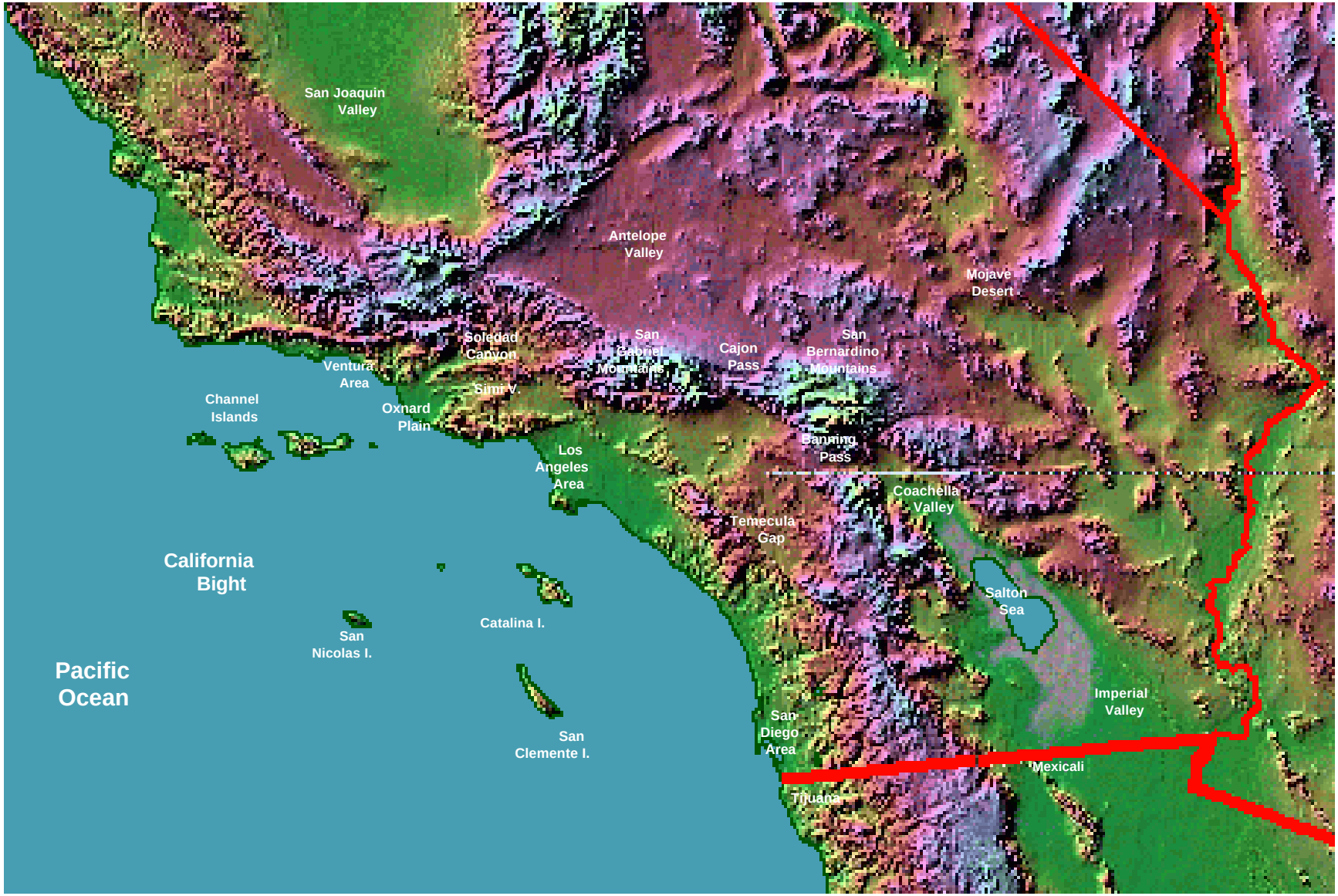

Figure 2-2. Topography of the SCOS97 study area.

Table 2-1
Population, Area and Emissions by County in SCOS97 Study Domain
1990

County	Air Basin	Population	Area Sq. Mi.	Emissions, Tons/Day TOG	ROG	CO	NOx
Kern	San Joaquin	480,572	5,580	350	210	380	210
Santa Barbara	South Central Coast	373,844	2,740	280	72	220	45
Ventura	South Central Coast	676,271	1,860	99	72	340	64
Los Angeles	South Coast	8,736,520	2,770	1,300	920	4,000	790
Orange	South Coast	2,451,688	770	530	290	1,300	220
Riverside	South Coast	910,857	1,850	150	90	440	81
San Bernardino	South Coast	1,172,907	1,140	260	130	530	110
Imperial	Southeast Desert	112,748	4,240	34	30	140	38
Kern	Southeast Desert	79,990	2,570	25	18	69	47
Los Angeles	Southeast Desert	219,628	1,300	44	25	130	30
Riverside	Southeast Desert	321,018	5,330	120	54	190	60
San Bernardino	Southeast Desert	302,196	18,980	180	51	200	150
San Diego	San Diego	2,546,751	4,260	530	300	1,400	200
	Air Basin Subtotals						
	San Joaquin	480,572	5,580	350	210	380	210
	South Central Coast	1,050,115	4,600	379	144	560	108
	South Coast	13,271,972	6,530	2,240	1,430	6,270	1,200
	Southeast Desert	1,035,580	32,420	403	180	729	320
	San Diego	2,546,751	4,260	530	300	1,400	200
	TOTAL	18,384,990	53,390	3,902	2,264	9,339	2,038

Table 2-2
1990 Daily Average ROG Emissions by Air Basins in SCOS97 Study Domain

	Air Basin					
Major Source Category	SJVAB (a)	SCCAB (b)	SoCAB	SEDAB	SDAB	Total
Fuel Combustion	11	2.5	15	4.6	2.5	36
Waste Burning	1.8	0.4	1.2	5.2	0.9	10
Solvent Use	14	32	420	29	76	571
Petroleum Processing, Storage & Transfer	120	33	96	3.6	8.2	260
Industrial Processing	1.1	0.6	41	2.5	2.9	48
Miscellaneous Processes	20	13	56	44	18	151
Miscellaneous	0	0	3.5	0	0	3.5
Stationary Sources	168	81	633	89	109	1,079
Light Duty Passenger	18	36	450	36	110	650
Light & Medium Duty Trucks	12	13	150	17	40	232
Heavy Duty Gas Trucks	1.8	2.2	30	5.4	6.8	46
Heavy Duty Diesel Trucks	3.7	2.1	21	9.1	3.8	40
Motorcycles	0.4	0.8	7.5	0.6	1.8	11
Diesel Urban Buses	0	0	1.6	0	0.3	1.9
On-Road Vehicles	36	54	660	68	163	981
Off-Road Vehicles	1.7	2.1	34	8.1	18	64
Trains	0.4	0.1	2.0	2.3		4.8
Ships		0.3	1.1		0.6	2.0
Aircraft - Government	0.4	0.4	7.6	5.4	2.1	16
Aircraft - Others	2.8	1.2	9.1	0.6	1.1	15
Mobile Equipment	1.8	3.2	56	3.2	2.5	67
Utility Equipment	0.9	1.9	22	1.8	4.3	31
Other Mobile	8	9	132	21	29	199
TOTAL	212	144	1,425	178	300	2,259

(a) Kern County only
(b) Santa Barbara and Ventura Counties

Table 2-3
1990 Daily Average NOx Emissions by Air Basins in SCOS97 Study Domain

	Air Basin					
Major Source Category	SJVAB (a)	SCCAB (b)	SoCAB	SEDAB	SDAB	Total
Fuel Combustion	140	24	200	57	22	443
Waste Burning		0.2	2.0	0.2		2
Petroleum Processing, Storage & Transfer	0.8		4.8		0.1	6
Industrial Processing		0.1	5.8	56		62
Miscellaneous Processes	0.2	1	3.3	0.3	1.1	6
Miscellaneous			1.3			1
Stationary Sources	141	25	217	114	23	520
Light Duty Passenger	13	28	290	28	74	433
Light & Medium Duty Trucks	10	12	110	14	32	178
Heavy Duty Gas Trucks	4.0	4.7	56	17	12	94
Heavy Duty Diesel Trucks	27	15	140	72	25	279
Motorcycles	0.1	0.3	1.8	0.1	0.4	3
Diesel Urban Buses	0.2	0	10		1.8	12
On-Road Vehicles	54	60	608	131	145	998
Off-Road Vehicles	0.3	1.0	10	0.9	4.8	17
Trains	8.8	3.3	42	46	0.6	101
Ships		1.5	33		9.8	44
Aircraft - Government	0.1	0.5	3.3	3.8	1.7	9
Aircraft - Others	0.4	0.6	15	0.5	2.5	19
Mobile Equipment	12	16	250	25	17	320
Utility Equipment		0.1	0.8	0.1	0.2	1
Other Mobile	22	23	354	76	37	511
TOTAL	216	108	1,179	321	205	2,029

(a) Kern County only
(b) Santa Barbara and Ventura Counties

from the study area in 1990 total 2259, 9339, and 2029 tons/day for reactive organic gases, carbon monoxide and nitrogen oxides, respectively (California Air Resources Board, 1993a), with 63 percent, 67 percent and 59 percent of those pollutants emitted within the SoCAB. Stationary sources and on-road mobile sources contribute equally to ROG emissions (45 and 46 percent, respectively) in the SoCAB, while mobile sources account for the majority of NO_X emissions (51% from on-road and 30% from nonroad). While these emission distributions also apply to total emissions for the entire study area, there are large regional differences in source contributions. Stationary sources account for the majority of ROG emissions in Kern County and the SCCAB, and for the majority of the NO_X emissions in Kern County.

Several other emissions that are not listed in Table 2-4 are important for understanding particulate and VOC concentrations in the SoCAB. Biogenic and geogenic emission rates are not included, and they can be significant. Biogenic ROG emissions in the SoCAB have been estimated to be 100 to 200 tons/day (Winer *et al.*, 1983; Horie *et al.*, 1990; Causley and Wilson, 1991), with substantial dependence on plant type, leaf biomass, wind speed, and temperature. Harley *et al.* (1993) used a value of 117 tons/day of biogenic ROG for ozone modeling of the August 27 to 29, 1987 SCAQS episode. This emission rate is comparable to those of many other source types in Table 2-2. Geogenic ROG emissions might be expected in areas where oil is extracted, but estimates of their magnitudes are not available.

These emission inventories provide a starting point for the updated 1997 emission inventory that will be required for the SCOS97 air quality modeling effort. Section 10 provides a summary of recent, current and planned projects that are related to development of the SCOS97 emission inventory, and an overview of emission inventory methodology and associated uncertainties.

2.2 Pollutant Transport and Summer Ozone Climatology

Given the primary emissions within the complex terrain of southern California, it is the climate of southern California that fosters generation of ozone, a secondary pollutant. High ozone concentrations most frequently occur during the "ozone season," spanning late spring, summer, and early fall when sunlight is most abundant. Meteorology is the dominant factor controlling the change in ozone air quality from one day to the next. Synoptic and mesoscale meteorological features govern the transport of emissions between sources and receptors, affecting the dilution and dispersion of pollutants during transport and the time available during which pollutants can react with one another to form ozone. These features are important to transport studies and modeling efforts owing to their influence on reactive components and ozone formation and deposition. This subsection provides a summary of meteorological features affecting southern California air quality, and provides a brief overview of the regulatory response to interbasin transport, i.e., the identification of "transport couples" and the characterization of the effect of transport on air quality in the receptor air basin. Specific transport studies are discussed in greater detail with the introduction of a conceptual model of ozone episodes and transport scenarios of interest in Section 2.6.

Southern California is in the semi-permanent high pressure zone of the eastern Pacific. During summer, average temperatures are ~25 ^{o}C, with maximum daily readings often exceeding 35 ^{o}C. Precipitation events are rare. Frequent and persistent temperature inversions are caused by subsidence of descending air which warms when it is compressed over cool, moist marine air. These inversions often occur during periods of maximum solar radiation which create daytime mixed layers of ~1,000 m thickness, though the top of this layer can be lower during extreme ozone episodes (Blumenthal *et al.*, 1978). Relative humidity depends on the origin of the air mass, proximity to the coast, altitude, and the time of day, and can exceed 50 percent during daytime throughout the SoCAB with the intrusion of a deep marine layer. Relative humidity is higher near the coast than farther inland (Smith *et al.*, 1984).

Several experiments and data analysis studies examined the relationship of meteorology to air pollutant transport pathways, diffusion, vertical mixing, and chemical transformation in the SoCAB (e.g., Edinger, 1959, 1973; Edinger and Helvey, 1961; Pack and Angell, 1963; Kauper and Hopper, 1965; Schuck *et al.*, 1966; Estoque, 1968; Lea, 1968; Stephens, 1968, 1969; Miller and Ahrens, 1970; Edinger *et al.*, 1972; Rosenthal, 1972; Shettle, 1972; Smith *et al.*, 1972, 1976, 1984; Drivas and Shair, 1974; Angell *et al.*, 1975, 1976; Kauper and Niemann, 1975, 1977; Husar *et al.*, 1977; Keith and Selik, 1977; Blumenthal *et al.*, 1978; McRae *et al.*, 1981; Witz and Moore, 1981; Farber *et al.*, 1982a, 1982b; McElroy *et al.*, 1982; Reible *et al.*, 1982; Sackinger *et al.*, 1982; Schultz and Warner, 1982; Shair *et al.*, 1982; Witz *et al.*, 1982; Smith and Shair, 1983; Cass and Shair, 1984; Smith and Edinger, 1984; Zeldin *et al.*, 1989; Douglas *et al.*, 1991; Bigler-Engler and Brown, 1995; Lea *et al.*, 1995). These experiments and others reveal several general features.

Smith *et al.* (1972), Keith and Selik (1977), and Hayes *et al.* (1984) describe wind flow patterns in the SoCAB. During summer, the sea-land breeze is strong during the day with a weak land-sea breeze at night. Owing to the high summer temperatures and extensive urbanization in the SoCAB, the land surface temperature does not usually fall below the water temperature at night, and nocturnal and morning winds are less vigorous than daytime winds. The land surface cools sufficiently to create surface inversions with depths as shallow as ~50 m. Surface heating usually erodes the surface and marine layers within a few hours after sunrise each day. Summertime flow patterns are from the west and south during the morning, switching to predominantly westerly winds by the afternoon. The land/sea breeze circulation moves air back and forth between the SoCAB and the Pacific Ocean, as well as along the coast to other air basins. Cass and Shair (1984) estimated that up to 50 percent of the sulfate measured at Lennox was due to emissions which had been transported to sea on the previous day. When wind speeds are low, air tends to slosh back and forth within the SoCAB.

In addition to these general features, there are many smaller features that affect the movement of pollutants within the SoCAB. Heating of the San Gabriel and San Bernardino Mountains during the daytime engenders upslope flows that can transport pollutants from the surface into the upper parts of, and sometimes above, the mixed layer. When the slopes cool after sunset, the denser air flows back into the SoCAB with pollutants entrained in it. Convergence zones occur where terrain and pressure gradients direct wind flow in opposite directions, resulting in an upwelling of air. Smith *et al.* (1984) have identified convergence zones at Elsinore (McElroy *et al.*, 1982; Smith and Edinger, 1984), the San Fernando Valley (Edinger and Helvey,

1961), El Mirage, the Coachella Valley, and Ventura. Rosenthal (1972) and Mass and Albright (1989) identified a Catalina Eddy, a counterclockwise mesoscale circulation within the Southern California Bight, as a mechanism for transporting air pollution. This eddy circulation transports pollutants from the SoCAB to Ventura, especially after the SoCAB ozone levels drop due to wind ventilation caused by an approaching low-pressure trough from the northwest. However, any southeast wind in southern California is initially capable of transporting polluted air consisting of ozone precursors and particulate matter from the SoCAB.

Blumenthal *et al.* (1978) describe the meteorology for a July 24 to 26, 1973, ozone case study during which the maximum hourly ozone average reached 630 ppb. During this episode, a strong high pressure ridge near the coast induced a cap of warm air over the SoCAB that limited the mixing depth for dispersing emissions. Nighttime surface inversions were strong and stable with little air movement until late morning. Ozone above the surface layer was not ventilated, and remained through the following day. The afternoon sea breeze was weak. On the second day, the surface layer increased in depth and entrained the ozone aloft with the ozone generated from fresh emissions. When the high pressure system weakened, the mixing depth increased and more vigorous on-shore winds ventilated the SoCAB.

General meteorological conditions and trajectories during the 1987 SCAQS episodes have been examined by Douglas *et al.* (1991). Flows during the summertime were westerly, and residence times were often less than 12 hours. The backward trajectories from Claremont and Riverside on August 27 and 28, 1987 show an upper level recirculation in the middle of the SoCAB that probably led to the build-up of ozone and precursors during this episode. Trajectories during SCAQS episodes were consistent with stagnation conditions desired for selecting episodes, and they provide confidence that the SCAQS forecasting methods can be successfully adapted to SCOS97 to evaluate high ozone episodes in the SoCAB. Summer episodes showed west to east transport with potential for pollutant carryover aloft. Forecasting methods for transport from the SoCAB to other air basins, or between other southern California basins, are more problematic and additional work will be needed to improve forecasting procedures.

Green *et al.* (1992a) classified wind field patterns in the SoCAB, San Joaquin Valley, and Mojave Desert during 1984 and 1985 to evaluate visibility reduction in the desert. This analysis evaluated transport between the SoCAB and the Mojave and Arizona deserts. Winds were found to be directly related to the pressure field, which, in summer, resulted from a consistent mesoscale component added to a varying synoptic-scale component. Three main summer patterns were found, all of which had some transport into the SEDAB from the SoCAB. The first, and predominant, pattern indicated typical summer conditions with the wind field driven by the ocean/interior temperature difference and terrain features. The second pattern typically occurred in early summer (May-early June), and had stronger flow into the desert due to synoptic-scale pressure gradients (upper level low pressure over the west coast, surface low over the Intermountain region). This type was also less stable due to cold air aloft. The third pattern showed weaker flow into the desert (and flow from the SEDAB to the SoCAB for a few hours per day) due to higher pressure to the northeast.

The predominant surface wind climatologies for California have been compiled for ARB by Hayes *et al.* (1984) based on 1977-1981 wind data. Figure 2-3 (after Hayes *et al.*) shows seven types of wind flow patterns for the SoCAB and the surrounding air basins. Not shown is an eighth possible condition of essentially calm winds. Table 2-4 gives the frequency of occurrence, expressed as a percentage, of each of these eight wind-pattern types for four times daily during each season. It should be noted that for certain times of day, particularly during the summer, southeast winds may be the predominant wind near and within the inversion (Lea *et al*, 1995; Fisk, 1996a, 1996b).

During summer (June-August) and fall (September-November), the Calm (Type VII), Offshore (Type III), and Downslope/Transitional (Type V) patterns dominate the early morning hours, allowing pollutants to accumulate in SoCAB industrial and business areas. Pollutants then move inland with the Sea Breeze (Type II) in the afternoon hours. However, a period of southeast flow towards Ventura County can occur as the land breeze veers to a daytime sea breeze. While this diurnal sequence is most common during the ozone season, other combinations of wind patterns occur that drive interbasin transport. For example, off-shore surface transport from the SoCAB to San Diego may occur with the Offshore winds (Type III), the Downslope/Transitional winds (Type V), and/or the Weak Santa Ana winds (Type VIa).

2.2.1 Transport Couples

The California Clean Air Act of 1988 required the Air Resources Board (ARB) to identify districts in which emissions and end-products transported from upwind areas outside the districts cause or contribute to exceedances of the state ozone standard within the district. The topography and wind climatology of California produce combinations of adjacent air basins, called "transport couples," where the upwind-downwind transport and emissions sources must be considered by regulators. This coupling effect has been clearly demonstrated, although not quantified, in southern California on a number of occasions through the use of tracer releases (e.g., Reible *et al.*, 1982; Smith and Shair, 1983) and other studies (e.g., Bigler-Engler and Brown, 1995; Lea *et al.*, 1995). The most significant transport couples have been identified (ARB, 1990b; ARB, 1993d) consistent with California wind flow patterns (Hayes *et al.*, 1984).

The impact of pollutant transport on the ozone air quality in a downwind basin is a function of the precursor emissions in the upwind basin, the losses of pollutants by deposition and reaction along the transport path, the formation of ozone along the transport path, the meteorological situation which transports and mixes the pollutants, and the local precursor emissions in the downwind basin. The geography of the region often influences the potential transport between air basins and the transport path. Since precursors are lost via reaction and deposition, the time of transport will have a significant influence on the amount of transported precursors still existing at the receptor site.

Given the difficult numerical problem of turbulence and diffusion in complex terrain, and given only limited resources for collection of meteorological and air quality data, *qualitative* characterizations of transport contributions to downwind exceedances have been defined in lieu of a more desirable but currently unattainable *quantitative* apportionment of upwind and downwind source contributions. These qualitative estimates are described as:

Figure 2-3 South Coast Air Flow Pattern Types

Table 2-4
South Coast Air Basin Airflow Types
Seasonal and Diurnal Percentages of Occurrence (1977-1981 Data)

Types	I	II	III	IV	V	VIa	VIb	VII
Time - PST	On-Shore South	Sea Breeze	Off-shore	Southerly	Downslope/ Transitional	Weak Santa Ana	Full Santa Ana (>20 kts)	Calm
Winter								
4 a.m.	3	3	25	3	17	10	7	29
10 a.m.	10	9	16	15	16	12	7	13
4 p.m.	24	51	4	11	4	4	2	0
10 p.m.	6	7	19	7	20	11	7	23
all times	11	18	16	9	14	9	6	16
Spring								
4 a.m.	10	8	19	6	26	4	3	24
10 a.m.	43	29	3	12	5	2	1	2
4 p.m.	31	61	2	4	1	1	1	*
10 p.m.	23	26	9	4	23	3	1	10
all times	27	31	8	6	14	3	2	9
Summer								
4 a.m.	10	5	4	4	34	1	1	37
10 a.m.	51	41	1	6	1	*	*	0
4 p.m.	26	73	0	1	0	0	0	0
10 p.m.	34	39	2	2	18	1	*	5
all times	30	40	2	3	13	1	*	11
Fall								
4 a.m.	7	10	16	2	26	7	4	25
10 a.m.	33	29	5	6	10	6	4	7
4 p.m.	20	67	4	2	2	1	1	4
10 p.m.	16	19	13	2	27	5	3	15
all times	19	31	10	3	16	5	3	13
Yearly								
4 a.m.	8	7	16	4	26	6	4	29
10 a.m.	34	27	6	10	8	5	3	6
4 p.m.	25	63	3	5	2	2	1	1
10 p.m.	20	23	11	4	22	5	3	14
all times	22	30	9	6	14	4	3	12

* < 0.5 percent

- *Overwhelming*. An ozone exceedance in the downwind area occurred with little or no emissions contribution from the downwind area. Transport alone caused the exceedance. An overwhelming transport day is also commonly called a "Transport Day."

- *Significant*. Emissions in the upwind air basin plus emissions in the recipient air basin contributed to the recipient's ozone exceedance. Both transported and local emissions are necessary to cause the exceedance. A significant transport day is also commonly called a "Shared Day."

- *Inconsequential*. Upwind emissions did not contribute to the exceedance in the recipient air basin. Local contribution alone caused the exceedance. An inconsequential transport day is also commonly called a "Local Day."

For this study, the most important transport couples previously identified by ARB are:

- SoCAB to the South Central Coast Air Basin (SCCAB, including Ventura and Santa Barbara).

- SoCAB to the Mojave Desert Air Basin (MDAB, the western and northern portions of the former Southeast Desert Air Basin, SEDAB).

- SoCAB to the San Diego Air Basin (SDAB).

- SCCAB to the SoCAB.

The reverse transport couples, i.e., SCCAB to SoCAB, MDAB (or SEDAB) to SoCAB, and SDAB to SoCAB, occur only occasionally, if at all, and they seldom result in high ozone concentrations in the SoCAB. Other transport couples influence air quality in several of the air basins surrounding the SoCAB, for example, transport from the San Joaquin Valley to the SEDAB and from Mexico to San Diego. While these transport couples are not directly studied in SCOS97, the study will include them indirectly via boundary measurements at the upwind edges of the modeling domain.

2.3 Transformation and Deposition

The role of VOCs in the formation of tropospheric ozone (O_3) has been well established (Seinfeld, 1986). The only significant chemical reaction producing ozone in the atmosphere is the reaction of atomic and molecular oxygen. While molecular oxygen (O_2) is abundant in the atmosphere, free oxygen (O) atoms are not. At lower altitudes, where only UV-radiation with wavelengths greater than 280 nm is present, the only significant oxygen atom production is from photodissociation of nitrogen dioxide (NO_2) into nitric oxide (NO) and atomic oxygen. NO reacts rapidly with ozone to regenerate NO_2. The first and third reactions occur rapidly, establishing a steady-state equilibrium ozone concentration that depends on the ratio of NO_2 to NO which in turn depends on the intensity of UV-radiation driving the photodissociation. One O_3 molecule is required to regenerate NO_2 from NO, so these reactions are insufficient, by

themselves, to create excessive ozone levels. When reactive organic gases are present, however, their oxidation produces hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2) which react with NO to form NO_2 without destruction of ozone, thereby allowing ozone to accumulate.

Other tropospherically important reactions involve oxides of nitrogen (NO_X, sum of NO and NO_2). The recombination reactions of OH with NO to form nitrous acid (HONO) and HO_2 and NO_2 to form pernitric acid ($HOONO_2$) do not affect the fate of NO_X because of the rapid photodissociation of HONO to OH radical and NO and the thermal decomposition of $HOONO_2$ back to reactants. HONO is also formed at night from the heterogeneous hydrolysis of NO_2, and is also directly emitted from combustion sources. The rapid photolysis of HONO in the early morning can lead to a rapid increase in the number of OH radicals and to rapid initiation of photochemical activity.

The reaction of OH with NO_2 to form nitric acid (HNO_3) is the major gas-phase sink for NO_2 in the troposphere. Reaction of HNO_3 with ammonia (NH_3) yields particulate ammonium nitrate (NH_4NO_3) and with sodium chloride (NaCl) to form sodium nitrate ($NaNO_3$) and hydrochloric acid (HCl). While $NaNO_3$ is associated with coarse particles (2 to 10 μm) and is stable, NH_4NO_3 is associated primarily with fine particles (less than 2 μm) and is in equilibrium with NH_3 and HNO_3 at typical summertime ambient temperatures in southern California.

Ozone also reacts with NO_2 to form nitrate (NO_3) radicals, and the NO_3 radical and NO_2 form an equilibrium with nitrogen pentoxide (N_2O_5). Because NO_3 radicals rapidly photolyze and react rapidly with NO, concentrations of the NO_3 radical, and N_2O_5 remain low during daytime but can increase during evening and nighttime hours in the absence of NO.

For the majority of VOCs emitted from anthropogenic and natural sources, reaction with the hydroxyl radical is the major cause of chemical change, and atmospheric lifetimes can be estimated from typical and maximum reaction rates for different organic compounds when the hydroxyl radical is present at urban concentrations. Typical lifetimes of some VOCs due to reaction with the hydroxyl radical are given in Table 2-7. This table shows that all the acetylene, most of the alkanes, benzene, and toluene have lifetimes which exceed the typical summer residence time of air masses during SCAQS (~12 hours according to SCAQS trajectories by Douglas *et al.*, 1991). Most of the other species in Table 2-7 will retain their relative abundances to other species when emissions are fresh (i.e., sampled within a few hours after release) but will have substantially changed in proportion to the other species after the air mass containing them has aged for a few hours. The degradation reactions for all classes of VOCs, in addition to the conversion of NO to NO_2 and the formation of ozone, lead to the formation of carbonyl compounds (aldehydes, ketones, hydroxycarbonyls, and dicarbonyls), organic acids, organic nitrates (including peroxylacyl nitrates, the simplest member of which is peroxyacetyl nitrate [PAN]). PAN thermally decomposes back to its reactants, NO_2 and acetylperoxy radical. Thus, like HONO, PAN can serve as a nighttime reservoir for NO_X and means of transport of NO_X to downwind areas. Recent measurements have indicated that carbonyl compounds that are produced from hydrocarbon oxidation can be important reactive VOCs themselves, and thus important sources of peroxy radicals responsible for ozone production (Martin *et al.*, 1991). Both the absolute concentrations of the carbonyl compounds, and the ratio of the product to the

Table 2-5
Typical Lifetimes of Some VOCs Due to Reaction with OH Radical

Compound	10E12 x k cm3/mol-sec @ 298 deg. K	Lifetimes Daytime 12-hour mean low		Lifetimes Daytime 12-hour mean high		Lifetimes Midday Peak	
OH/cm3		5.0E+05		5.0E+06		1.0E+07	
Alkanes							
Methane	0.00836	15.2	years	1.5	years		
Ethane	0.268	173	days	17.3	days		
Propane	1.15	40	days	4.0	days		
n-Butane	2.54	18	days	1.8	days		
2-Methylpropane (i-Butane)	2.34	20	days	2.0	days		
n-Pentane	3.94	12	days	1.2	days		
2-Methylbutane (i-Pentane)	3.90	12	days	1.2	days		
n-Hexane	5.61	8.3	days	9.9	hours	5.0	hours
2-Methylpentane	5.6	8.3	days	9.9	hours	5.0	hours
3-Methylpentane	5.7	8.1	days	9.7	hours	4.9	hours
2,4-Dimethylpentane	5.1	9.1	days	10.9	hours	5.4	hours
Heptane	7.2	6.5	days	7.8	hours	3.9	hours
Methylcyclohexane	10.4	4.5	days	5.3	hours	2.7	hours
Alkenes							
Ethylene	8.5	5.4	days	6.5	hours	3.3	hours
Propene	26.3	1.8	days	2.1	hours	1.1	hours
Butene	31.4	1.5	days	1.8	hours	0.9	hours
cis-2-Butene	56.1	9.9	hours	1.0	hours	0.5	hours
trans-2-Butene	63.7	8.7	hours	0.9	hours	0.4	hours
3-Methyl-1-Butene	31.8	1.5	days	1.7	hours	0.9	hours
Cyclohexene	67.4	8.2	hours	0.8	hours	0.4	hours
Isoprene	101.0	5.5	hours	0.6	hours	0.3	hours
Alkynes							
Acetylene	0.9	51.4	days	5.1	days		
Aromatics							
Benzene	1.2	37.6	days	3.8	days		
Toluene	6.0	7.8	days	9.3	hours	4.7	hours
m-Xylene	23.6	2.0	days	2.4	hours	1.2	hours
p-Xylene	14.3	3.2	days	3.9	hours	1.9	hours
o-Xylene	13.7	3.4	days	4.1	hours	2.0	hours
Ethylbenzene	7.1	6.5	days	7.8	hours	3.9	hours
1,2,4-Trimethylbenzene	32.5	1.4	days	1.7	hours	0.9	hours

Lifetimes are for summer conditions. Lifetimes in winter are about 3-4 times longer.
Rate constants from Atkinson (1989)

parent hydrocarbon can provide useful information regarding the extent of hydrocarbon oxidation chemistry occurring in a particular air mass.

The reactive nitrogen compounds (NO_y), NO, NO_2, NO_3, N_2O_5, $CH_3COO_2NO_2$ (PAN), HNO_3, HONO, and other organic nitrogen-containing species are coupled by a complex sequence of reactions in the atmosphere which generate ozone, other oxidants, organic and inorganic acids, and various hydrocarbon oxidation products. Because the amount of NO_y in a given air mass is dependent only on the sources and sinks of its component species and not on interconversion chemistry, NO_y is a conserved quantity. Thus, NO_y is a measure of the amount of nitrogen containing "pollution", independent of the air mass's age. It is NO_y rather than NO_X that is of primary interest in establishing the nitrogen budget across a transport flux plane. In addition, our understanding of the reaction pathways which involve nitrogen species can be aided by the measurement of the total abundance of atmospheric reactive compounds.

Much of the difficulty in addressing the ozone problem is related to ozone's complex photochemistry. The rate of O_3 production is a non-linear function of the mixture of VOC and NO_X in the atmosphere. Depending upon the relative concentration of VOC and NO_X and the specific mix of VOC present, the rate of O_3 formation can be most sensitive to changes in VOC alone or to changes in NO_X alone or to simultaneous changes in both VOC and NO_X. Understanding the response of ozone levels to specific changes in VOC or NO_X emissions is the fundamental prerequisite to developing a cost-effective ozone abatement strategy, and is the principal goal of SCOS97-NARSTO.

2.4 Spatial and Temporal Ozone Patterns

In a modeling study, Ireson and Hogo (1983) generated expected contours of peak ozone concentrations in the SEDAB. Smith and Shair (1983) have provided contour plots from ozone measurements on transport days during the tracer study of summer 1981 showing the spatial distribution of ozone in the SoCAB and the SEDAB. Figure 2-4 (from Stoeckenius *et al.,* 1991) shows functional grouping of sites within the SoCAB that exhibit similar ozone time series. Stoeckenius *et al.* (1991) describe the similarities between the sites in each of the following nine functional groups:

1. North Coast (West LA, Hawthorne, N. Long Beach)
2. South Coast (Los Alamitos, Costa Mesa)
3. Metropolitan (Los Angeles, Lynwood, Anaheim)
4. San Fernando Valley (Burbank, Reseda)
5. San Gabriel Valley (Pasadena, Azusa, Glendora)
6. Inland Metropolitan (Pico Rivera, Whittier, La Habra)
7. Inland Foothill (Pomona, Upland, Fontana)

Figure 2-4 Sites within SoCAB that exhibit similar ozone time series

8. Inland Valley (San Bernardino, Redlands, Riverside)

9. Mountain (Newhall, Lake Gregory)

During the most typical summer conditions (corresponding to Scenario #3 introduced in Section 2.5), the maximum ozone concentrations experienced in the SoCAB are in the San Gabriel Valley group. A "Southern Route" pattern (Section 2.5, Scenario #1) produces the greatest ozone along the North and South Coast as well as in the Metropolitan and Inland Metropolitan functional groups. The Eddy Pattern (Section 2.5, Scenario #4) tends to produce higher relative ozone concentrations in the San Fernando Valley and at both the Mountain sites.

Table 2-6 lists the number of state, federal, and first stage health advisory exceedances for the 1990-93 ozone seasons that have occurred at each monitoring station in the Mojave Desert, South Central Coast (Ventura and Santa Barbara), and San Diego Air Basins and for selected SoCAB monitoring stations (one from each functional group after Stoeckenius *et al.*, 1991). The temporal pattern of exceedances in the Mojave Desert closely follows that of the SoCAB, while a relationship with the other three areas — Ventura, Santa Barbara, and San Diego — is less clear. Downtown San Diego (sites SD 123 & 138) exhibit a bimodal distribution with the majority of exceedances occurring in the fall. The elevated Alpine site, on the other hand, more closely follows the SoCAB distribution and has the worst ozone air quality in San Diego.

2.5 Conceptual Model of Ozone Episodes and Transport Scenarios of Interest

As part of the SCOS97 effort, the Meteorological Working Group has formed five scenarios of ozone episodes which include suspected accompanying interbasin transport. Figure 2-5 shows the suspected transport pathways for the following five types of ozone episodes and transport scenarios, listed in order, as prioritized by the Meteorological Working Group:

1. *SoCAB Ozone Maximum*. SoCAB pollutants remain trapped within SoCAB. There may be "local" exceedance days for other basins. This condition may be accompanied by a "coast hugger," a near-coast flow of SoCAB pollutants toward the southeast.

2. *Upper-level transport to San Diego Air Basin*. Ozone in a layer 300-500 m MSL above the marine layer or above the nocturnal inversion jets southeast toward San Diego. The centerline and width of this pathway are uncertain, and may range from the Interstate 15 route (east) to an off-shore route (west).

3. *Secondary SoCAB Maximum*. An on-shore breeze causes inland transport, with likely transport into the Mojave Desert. This situation may also correspond to local exceedances for Ventura, Santa Barbara, and San Diego Counties.

4. Coastal Day with Eddy. This is an extended SoCAB episode that ends with a southeast wind offshore, over the basin, and even sometimes in the desert. It is possibly an extension of Scenario #1 or #2. The ozone peaks are often seen at Newhall or Simi Valley on these days.

Table 2-6
Southern California Ozone Standard Exceedances for June-October 1990-93

	June			July			Aug			Sept			Oct		
APCD or AQMD	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage
South Coast															
Hawthorne	2/120	0	0	1/124	0	0	4/121	0	0	8/120	0	0	7/124	0	0
Los Alamitos	13/120	3/120	1/120	6/124	2/124	1/124	17/124	2/124	0	29/119	10/119	5/119	21/123	5/123	3/123
Los Angeles	30/120	11/120	3/120	39/123	15/123	4/123	38/124	14/124	5/124	50/114	21/114	9/114	30/121	12/121	3/124
Burbank	56/118	21/118	12/118	65/124	34/124	19/124	74/123	36/123	20/123	61/116	30/116	13/116	43/122	19/122	6/122
Azusa	71/119	47/119	35/119	95/124	59/124	40/124	101/124	72/124	50/124	93/119	71/119	45/119	49/123	34/123	23/123
Pico Rivera	38/118	18/118	10/118	53/120	24/120	17/120	70/123	33/123	20/123	78/120	47/120	33/120	45/124	26/124	14/124
Pomona	56/120	29/120	23/120	78/124	43/124	29/124	83/124	47/124	37/124	79/119	47/119	29/119	39/124	27/124	17/124
San Bernardino	68/120	38/120	31/120	91/124	59/124	38/124	95/124	57/124	47/124	90/120	55/120	41/120	42/122	27/122	20/122
Lake Gregory	93/120	69/120	49/120	117/123	94/123	72/123	115/124	92/124	69/124	94/120	59/120	39/120	36/122	12/122	4/122
Ventura															
Piru	12/	1/118	0	16/124	0	0	24/124	1/124	0	18/120	3/120	1/120	19/124	1/124	0
Ojai	19/120	1/120	0	10/119	1/119	0	26/124	0	0	16/120	2/120	1/120	20/124	3/124	0
Simi Valley	27/120	5/120	1/120	54/124	8/124	1/124	70/124	16/124	3/124	47/120	16/120	6/120	32/124	8/124	0
Ventura	4/111	0	0	0/124	0	0	2/124	1/124	0	6/120	0	0	5/123	0	0
Thousand Oaks	13/120	1/120	1/120	2/122	0	0	13/122	1/122	0	23/120	3/120	0	18/124	0	0
El Rio	5/119	0	0	2/119	0	0	6/124	0	0	5/120	0	0	9/124	0	0
Santa Barbara															
Carpenteria	4/120	0	0	4/114	1/114	0	3/124	0	0	4/117	0	0	3/124	0	0
Santa Ynez	1/119	0	0	2/124	0	0	0	0	0	1/119	0	0	4/124	0	0
Loma Poc	0	0	0	1/110	0	0	0	0	0	0	0	0	1/123	0	0
Santa Maria	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Goleta	1/119	0	0	3/124	0	0	1/121	0	0	3/120	0	0	3/121	0	0
El Capitan	1/120	0	0	2/124	0	0	0	0	0	1/118	0	0	2/124	0	0
SB 388	1/118	0	0	5/124	1/124	0	0	0	0	0	0	0	3/123	0	0
SB 401	1/120	0	0	1/124	0	0	0	0	0	1/120	0	0	1/124	0	0

Table 2-6 (continued)
Southern California Ozone Standard Exceedances for June-October 1990-93

	June			July			Aug			Sept			Oct		
APCD or AQMD	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage	State	Federal	1st Stage
Mojave Desert															
29 palms	45/120	1/120	0	34/124	3/124	0	20/94	0	0	May-89	0	0	Mar-93	0	0
Victorville	64/119	13/119	4/119	76/123	22/123	10/123	56/122	12/122	4/122	24/120	2/120	0	6/118	0	0
Trona	7/107	0	0	Apr-78	0	0	3/100	0	0	Feb-97	0	0	0	0	0
Phelan	81/119	46/119	25/119	106/124	69/124	38/124	96/124	47/124	23/124	54/120	19/120	6/120	15/119	5/119	0
Hesperia	85/120	45/120	18/120	102/122	47/122	26/122	95/109	46/109	21/109	65/117	21/117	9/117	17/124	2/124	1/124
Barstow	25/112	0	0	36/121	4/121	0	22/99	0	0	Jul-88	0	0	1/123	0	0
San Diego															
Oceanside	4/120	0	0	0	0	0	1/123	0	0	11/119	5/119	3/119	16/122	5/122	2/122
Escondido	9/120	2/120	1/120	5/124	0	0	10/124	1/124	0	20/120	4/120	2/120	22/124	7/124	4/124
SD 123	9/120	4/120	1/120	2/122	0	0	3/111	1/111	0	20/111	5/111	2/111	21/121	9/121	5/121
SD 138	6/120	0	0	1/124	0	0	1/124	0	0	10/120	1/120	0	18/124	7/124	4/124
Delmar	5/118	1/118	0	0	0	0	2/124	1/124	0	14/120	4/120	2/120	26/123	9/123	2/123
Chula Vista	4/120	1/120	1/120	1/124	0	0	1/124	0	0	16/119	3/119	1/119	18/124	5/124	1/124
El Cajon	18/120	3/120	3/120	10/124	1/124	0	16/124	0	0	21/120	3/120	0	30/124	4/124	0
Alpine	48/120	11/120	3/120	58/124	5/124	1/124	63/124	14/124	2/124	58/120	11/120	3/120	46/124	10/124	2/124
El Centro	14/120	1/120	0	3/122	0	0	0	0	0	3/120	1/120	1/120	5/124	0	0

Figure 2-5 Possible transport corridors for transport couples of interest

5. *Off-shore surface transport direct to the San Diego Air Basin.* This event is characterized by a mild Santa Ana wind condition followed by the on-shore flow. It occurs with greatest frequency later in the ozone season (September-October).

These five scenarios comprise the core of a conceptual model. In practice, there may be overlap between the scenarios. For example, also related to the Santa Ana winds discussed in Scenario #5 are subsequent periods of southeast flow which cause transport to the South Central Coast Air Basin as discussed in Scenario #4. Mild Santa Ana winds may be associated with *simultaneous* transport from southern portions of SoCAB to SDAB and from northern portions of the SoCAB to the SCCAB. (See wind-pattern type VIa in Figure 2-3.) The sampling network should be designed to accommodate potential overlap. Each scenario and relevant past studies are discussed in the following five subsections.

2.5.1 SoCAB Ozone Maximum

Stoeckenius et al. (1991) have studied days when SoCAB pollutants remain trapped within the SoCAB. Pollutants may move back and forth in a weak land/sea breeze. This situation is characterized by "sloshing" of pollutants back and forth. This phenomena is sometimes called "recirculation," though recirculation better describes a simultaneous return flow aloft. This scenario may also lead to a "coast hugger" or "Southern Route Day" because of the near-coast flow of pollutants toward the southeast.

These days are characterized by high 850-mb temperatures, weak offshore surface pressure gradients (higher pressure to the north or northeast) and an upper level ridge inland from the Pacific Coast. Weak off-shore flow during night and morning hours and on-shore flow in the afternoon, combined with low mixing depths gives low dispersion and high concentrations near the coast and in nearby valleys. A period of southeast flow between the night-time land-sea breeze and the daytime sea-land breeze may cause transport to Ventura County and beyond. (See wind-pattern type V in Figure 2-3.) Subsidence aloft, enhanced by downslope flow over the mountains, causes warm temperatures aloft and results in low mixing heights throughout the Los Angeles Basin. Afternoon mixing heights may be only 500-700 feet at inland locations. This pattern can be forecast using prognostic maps from the National Meteorological Center (NMC) models, such as the NGM and ETA models. Weak upper air gradients, with an upper high inland of the Pacific Coast, and surface pressure slightly higher to the northeast of the SoCAB predicted by the models should result in these conditions.

2.5.2 Upper-Level Transport to San Diego Air Basin

Under this scenario, it is hypothesized that transport from the South Coast Air Basin (SoCAB) occurs in the layer just above the marine layer and then may be mixed to the surface during the late morning or early afternoon due to diurnal heating in inland portions of the San Diego Air Basin (SDAB). In the Los Angeles to San Diego Three-Dimensional Ozone Transport Study, Kauper and Niemann (1977) noted that on many days during which trajectories based upon surface winds would indicate ozone from San Diego area sources, ozone and wind data aloft suggested that sources in the SoCAB may have been responsible for high ozone levels in the

SDAB. Kauper and Niemann speculated that under typical summertime conditions, northwesterly flow (i.e., flow *from* the northwest) aloft would transport elevated ozone layers from SoCAB toward the SDAB. They also suggested that surface heating would mix ozone to the ground, but questioned whether the high surface concentrations measured at some locations could result only from ozone layers aloft mixing to the surface. They suggested that mixing layers aloft to the surface would dilute the ozone to lower levels than those measured at the surface sites.

The San Diego Air Quality Study (SDAQS) was conducted during the summer of 1989 (Bigler-Engler and Brown, 1995; Hossain and Kaszuba, 1995). The objective of the SDAQS was to provide a high quality database for air quality simulation modeling and development of control strategies. Analysis of data from one study episode shows that ozone and its precursors from the SoCAB were transported overnight and in the early morning and that these pollutants fumigated to the surface in the San Diego Air Basin at multiple sites. The data from the study indicate that these transported pollutants can play a key role in ozone episodes in the SDAB.

Bigler-Engler and Brown (1995) report on a case of high ozone concentrations at Alpine (42 km east of downtown San Diego) during the SDAQS that initially appeared, based on surface winds, to be due to San Diego area (local) emissions. During this September 26, 1989 case, transport within the lowest few hundred meters above the surface was from the coast to inland; this seemed to imply high concentrations at Alpine due to transport from San Diego. However, ozone levels in San Diego remained low, and ozone at Alpine increased dramatically in the hour from 10 am to 11 am. This rapid increase during late morning, coinciding with deepening of the mixed layer due to solar insolation, suggested that fumigation from aloft was primarily responsible for the high concentrations (0.17 ppm) observed at Alpine. Direct advection into elevated terrain may also play a role. Vertical wind profiles showed transport from the northwest over night on September 25-26 and into mid-morning on September 26. This implicated the South Coast Air Basin as the predominant source of the high ozone recorded at Alpine, according to Bigler-Engler and Brown (1995).

The meteorological conditions that may lead to ozone transport aloft from the SoCAB to the SDAB may be hypothesized. If the synoptic scale flow leads to light north-northwesterly transport above the marine layer, then ozone layers that have been lifted aloft in the SoCAB may then be transported toward the SDAB, where they may be mixed to the surface in inland SDAB sites during midday due to solar insolation-caused deepening of the mixed layer. Direct advection of SoCAB air into elevated terrain in the SDAB may also contribute to high ozone at Alpine. The mechanisms for formation of ozone layers aloft in the SoCAB (slope flows, undercutting by the sea-breeze, upward motion in convergence zones, and transport into the inversion layer by convective elements) are described by Smith and Edinger (1984) and McElroy and Smith (1993). Thus, under periods of light north-northwesterly flow aloft, such as with a 500-mb ridge over or off the west coast and higher surface pressure to the north or northwest, elevated layers may be transported aloft overnight from the SoCAB and mixed to the surface at inland locations the following day in the SDAB.

2.5.3 Secondary SoCAB Ozone Maximum

This scenario occurs with an on-shore breeze causing inland transport and represents the typical summer day. The SoCAB is ventilated when air exits to the Mojave Desert and the Coachella Valley (Green *et al.*, 1991, 1992b). With weak synoptic gradients, the mesoscale effects of the seabreeze and the thermal low over the desert dominate the transport. This scenario often causes violation of the ozone standard at inland areas of the SoCAB and may be associated with locally caused violations in Ventura, Santa Barbara, and San Diego Counties. Due to the transport into the Mojave Desert during the late afternoon and evening, this scenario may also be expected to cause violations at Victorville and Palmdale. Green *et al.* (1992b) found that transport of visibility reducing pollutants into the Mojave Desert from the SoCAB was greatest for typical summer days.

This scenario is especially important for the SoCAB/SEDAB transport couple. Several studies have shown that high ozone levels in the SEDAB result primarily from transport of ozone and precursors from the SoCAB (e.g., Shettle, 1972; Smith *et al.*, 1972, 1976, 1984; Drivas and Shair, 1974; Angell *et al.*, 1976; Reible *et al.*, 1982; Shair *et al.*, 1982; Smith and Shair, 1983; Cass and Shair; 1984; Smith and Edinger, 1984; Raudy, 1990; Tilden *et al.*, 1991; Roberts *et al.*, 1992; ARB, 1990b, 1993d; Keislar *et al.*, 1994; Keislar and Schorran, 1995). The time of maximum ozone concentrations is progressively later at sites located at increasing distances from the coast (Smith *et al.*, 1983), which is consistent with the timing of transport from the SoCAB to the SEDAB. Smith *et al.* found that high morning ozone levels in the desert were usually associated with transport during the previous afternoon and night. Increases from the morning minimum to daily maximum averaged 30-40 ppb regardless of absolute concentration, suggesting that carryover of pollutants contributed to high baseline levels, but did not provide additional reactive material.

Using tracer releases, pollutants have been shown to travel from the SoCAB into the SEDAB through Cajon, San Gorgonio (Banning), and Soledad passes (Drivas and Shair, 1974; Angell *et al.*, 1976; Reible *et al.*, 1982; Smith and Shair, 1983). Smith and Shair (1983) also found evidence of transport aloft from the San Fernando Valley into eastern Ventura County under certain circumstances. Perfluorocarbons, methylchloroform, and hydrocarbons were also measured in canisters on ARB and Project MOHAVE aircraft. The halocarbon methylchloroform is primarily emitted within the SoCAB (Bastable *et al.*, 1987) and has been used to identify the influence of SoCAB air on downwind sites in California, Nevada, and Arizona (Rogers *et al.*, 1987; Miller *et al.*, 1990; Schorran *et al.*, 1990; White *et al.*, 1990; Pryor and Hoffer, 1991; Keislar *et al.*, 1994).

During summer 1992, several radar wind profilers were used in the SEDAB and in the eastern SoCAB. The NOAA Environmental Technology Laboratory, operators of the 1992 southern California radar wind profiler (RWP) network, drew the following conclusions (NOAA, 1994) about SoCAB-to-SEDAB transport:

- Daytime winds in the lowest 500 to 1000 meters AGL showed nearly continuous transport from the SoCAB to the SEDAB at Cajon and Banning passes.

- While synoptic scale weather patterns had little effect on winds in the SoCAB and SEDAB, they affected mixing depths, which were in turn related to 500-mb heights and ozone concentrations at San Bernardino.

- When mixing heights at San Bernardino rose above the height of Cajon Pass, and good transport occurred through the pass, ozone violations were likely at Hesperia.

- During high ozone days at Barstow, CA, in the interior of the Mojave Desert, flow was directly from Cajon Pass; on low ozone days, flow from Cajon Pass was transported south of Barstow, and flow from Tehachapi Pass (from the San Joaquin Valley) remained north of Barstow.

During the summer months, ozone concentrations in Barstow regularly exceed the 0.09 ppm California standard. While the majority of these exceedance days can be directly attributed to transport from the SoCAB, the cause of some exceedances is less straightforward (Roberts *et al.*, 1992). Analyses performed by ARB (1990b, 1993d) directly support inconsequential transport and the existence of two locally generated Barstow ozone exceedances (i.e., generated from emission sources within the SEDAB only). Based on this analysis, the ARB proposed rule-making for stationary sources within the MDAB.

However, controversy surrounded the ARB conclusion. The Mojave Desert Air Pollution Transport Committee (MDAPTC) was established by the ARB in December 1993 to bring together the regulating, regulated, and scientific communities to evaluate the existing evidence from past studies and to present conclusions and recommendations to the Board. The MDAPTC found no clear indication of local ozone formation. However, the MDAPTC did not reach consensus on which of the studies provided the most valid evidence that emissions from within the desert did not cause or contribute to exceedances of the state ozone standard in the desert. This lack of consensus was due, in part, to the fact that most past studies focused on transport episodes and not on the local contribution. No one study was deemed conclusive of the existence or not of locally caused exceedances of the state standard, and the conclusions of those few studies which address the issue of local generation are conflicting (MDAPTC, 1996). Thus, the MDAPTC recommended further studies which include:

- The 1995 Mojave Desert Transport Study conducted by ARB. Measurements taken during May-October 1995 included enhanced surface monitoring in suspected transport corridors, mountain top monitoring for ozone aloft, two radar wind profilers. During August, the NOAA ozone lidar with 2D scanning mode capability was deployed with a radar wind profiler and aircraft measurements were taken. Data validation is underway, with reports expected by the end of 1996.

- The Barstow Halocarbon Study was designed to provide a complementary characterization of the SoCAB influence on Barstow ozone by using halocarbon tracers of opportunity (methylchloroform and perchloroethylene) to detect the presence or absence of SoCAB (and possibly SJVAB) air in Barstow. The study period was August 1994 through October 1995, which included the time period for the 1995 Mojave Desert Transport Study.

This scenario should be easy to forecast. It occurs frequently and is associated with a thermal low over the lower Colorado River Valley and a surface high pressure over the eastern Pacific Ocean. The main exceptions to this pattern are conditions of offshore pressure gradients (Santa Ana winds), which are most likely late in the ozone season, and synoptic scale low pressure over the Great Basin, which occurs typically in late spring. Weak Santa Ana conditions lead to high ozone near the coast and prevent substantial transport into the Mojave Desert, whereas the Great Basin low results in good dispersion due to enhanced vertical mixing and relatively strong winds (Green *et al.,* 1992b).

2.5.4 Coastal Day with Eddy

Typically a few times each summer, the usual westerly to northwesterly low-level winds near the Pacific Coast in southern California become south to southeast and are accompanied by an increased depth of the marine layer and an increase in low-level stratus. These conditions are typically associated with a cyclonic eddy, named the "Catalina Eddy," centered over the Southern California Bight. Because of the change in wind, mixing depths, and cloud cover, ozone concentration fields during eddy events may be expected to differ substantially from typical summer patterns. During the mature phase of the eddy, the increased marine layer depth (up to 3000 m) and lack of sunshine required for ozone formation would tend to result in relatively low ozone levels. However, at the beginning of an eddy event, as the southeasterly coastal winds begin, and before full development of the eddy, air with high ozone concentrations may be transported to the northwest. This scenario has been considered in a review of air pollution transport mechanisms affecting Ventura County (Lea *et al.*, 1995). It should be noted that even on days with no obvious eddy circulation, there is often a shear zone and region of cyclonic curvature to the wind flow offshore. Also, a tendency for southeast flow in late morning is typically observed for at least a few hours. Thus, transport toward the South Central Coast may occur even without a discernible, closed eddy circulation (Rosenthal, 1972).

Wakimoto (1987) presents a case study of a Catalina Eddy (August 8-10, 1984) that occurred during Project BASIN, which included enhanced surface and upper air monitoring. Ozone concentrations at nine locations are presented for the period. On August 8, prior to the eddy, high ozone concentrations (up to 0.31 ppm at Glendora) occurred at Glendora, Newhall, and Banning. Ozone at these sites decreased substantially during the eddy. However, ozone to the northeast of Los Angeles at Simi Valley, Thousand Oaks, and Goleta (near Santa Barbara) increased as eddy winds transported pollutants into these areas. Interestingly, at El Rio, just inland from Ventura, ozone levels did not increase; presumably due to inland penetration of the sea-land breeze resulting in less transport of ozone and its precursors. Wakimoto speculated that the high ozone concentrations at Goleta were due to transport above the sea-breeze front and mixing to the ground. Different mixing processes in the coastal zone could explain why increased ozone was observed at Goleta, but not at El Rio. A limitation of the Wakimoto analysis is that it is applied to only one case of a Catalina Eddy, which may or may not represent typical ozone patterns associated with the Catalina Eddy.

Mass and Albright (1989) produced averaged fields of wind, pressure, and other variables for 50 Catalina Eddy events in the 15-year period 1968-1982. Their criteria for a Catalina Eddy

included a southerly surface wind component at San Diego of 1.5 m/s or more for 18 hours, and with at least 4 of those hours having a southerly component of 4 m/s or greater. The months used were May-September. Mass and Albright give a hypothesis for the mechanisms causing the Catalina Eddy and describe what features to look for using output from operational weather forecasting products from the National Meteorological Center. Unfortunately, Mass and Albright did not present averaged ozone concentration fields to correspond to their averaged pressure and wind fields.

According to Mass and Albright, during the eddy events, a 500-mb trough enters the Pacific Northwest from the eastern Pacific Ocean and broadens and deepens to the south along the coast. At 850 mb, the trough over the southwestern United States deepens and the Pacific High builds, causing an increase in the east-west pressure gradient. At the surface, the thermal low expands northwestward into the Central Valley of California. The increased pressure gradients cause strong northerly winds over the San Rafael Mountains north of Santa Barbara. These winds initiate the formation of a lee trough over the ocean south of Santa Barbara. Higher pressure to the south causes an ageostrophic flow from south to north near the coast. Because nearly geostrophic northerly winds are occurring further offshore, cyclonic vorticity is generated, thus forming the Catalina Eddy.

Mass and Albright found that the Catalina Eddy is often preceded by high pressure at the surface and aloft over the Great Basin or Rocky Mountains. This may be expected to give weak Santa Ana conditions with the potential for buildup of ozone in the SoCAB, which may then be transported as a "blob" toward the South Central Coast Air Basin during the early stages of the Catalina Eddy that follows.

Mass and Albright state that the above described 500-mb, 850-mb, and surface pressure patterns leading to Catalina Eddies are well forecasted a day in advance by the Nested Grid Model (NGM). Presumably, the ETA model, which is slated to replace the NGM will also do a reasonable job at predicting conditions leading to the formation of the Catalina Eddy. The high-resolution Navy Operational Regional Atmospheric Predictions System (NORAPS) and other follow-on forecast models developed by the Naval Research Laboratory may also be available for SCOS97. The NORAPS model has shown good potential for forecasting Catalina Eddy circulation.

Transport aloft from the SoCAB toward the SCCAB may occur frequently in summer without a noted eddy circulation. Lea *et al.* (1995) point out that in the late spring to early autumn, the predominant wind directions at 1000-3000 feet MSL during the night and morning hours are from the southeast over near coastal locations of the SoCAB and SCCAB (Point Mugu, Laguna Peak, El Monte, Los Angeles Airport, and Santa Monica). Ozone and precursors injected into the elevated inversion layer during the previous day thus may be frequently transported toward the northwest into the South Central Coast Air Basin. If a mechanism exists to transport this ozone to the surface, such as diurnal heating, then high surface concentrations could result in the SCCAB. This would appear to be most likely at inland locations that experience significant heating prior to arrival of the seabreeze front.

2.5.5 Off-Shore Surface Transport Direct to San Diego Air Basin

This transport scenario considers offshore transport from the SoCAB to the San Diego Air Basin at low levels. During weak Santa Ana conditions, light flow from the north to northeast in the Los Angeles area transports ozone and precursors offshore. As pressure gradients weaken and become onshore during the daytime, the polluted layer may then be transported onshore in the San Diego Air Basin (SDAB). Surface pressure gradients within the SoCAB undergo a diurnal pattern. During late afternoon, pressure gradients between coastal areas and inland areas reach a relative maximum. Under weak Santa Ana conditions, offshore flow occurs from evening through mid-morning. During mid-afternoon, in spite of offshore synoptic scale gradients, weak onshore seabreeze flows may occur. This may cause very high ozone concentrations in the SoCAB. If offshore gradients intensify slightly, pollutants may be transported offshore toward San Diego. They can then be brought onshore with the seabreeze in San Diego when coast to inland gradients in the SDAB become favorable for onshore flow. It may be that only slight variations in the synoptic pressure gradients lead to significant changes in the mesoscale transport and distribution of ozone, complicating the forecasting and modeling of ozone concentrations. Under these conditions, high ozone concentrations may occur anywhere within the SDAB (Bigler-Engler and Brown, 1993)

Kauper and Niemann (1977), Bigler-Engler and Brown (1995) and others have shown the SoCAB to be the main source of high ozone concentrations in the SDAB associated with weak Santa Ana conditions. Also, during weak Santa Ana winds or immediately following them, there is often a period of southeast flow causing transport in the opposite direction, towards the South Central Coast.

2.6 Requirements for Data Analysis and Modeling

The data required for this study are primarily driven by the need to drive and evaluate the performance of modeling systems. In evaluating the model performance, the primary concern is replicating the physical and chemical processes associated with actual ozone episodes. This necessitates the collection of suitable emissions, meteorological, and air quality data that pertain to these episodes. This section describes the data requirements of meteorological and air quality models.

2.6.1 Meteorological Modeling

The specification of the meteorological fields which drive the transport and dispersion of atmospheric pollutants is the critical component in mesoscale air quality modeling. The primary objective is to obtain wind fields over the model grid and determine mechanical and convective mixing depths. The simplest way is to use field measurements and interpolate the values over the entire domain. However, field measurements are generally spatially and temporarily sparse, and can be especially inadequate in areas with complex terrain and land-sea interactions such as southern California. Another way is to use diagnostic and prognostic meteorological models to estimate meteorological fields from existing data and then to adjust these fields through parameterizations of physical processes. Transport and dispersion of atmospheric pollutants is

governed by the dynamics and thermodynamics of the atmospheric boundary layer (ABL). The main difficulties in dispersion estimates arise with topographic complexity and increasing atmospheric stability. Turbulence in the ABL is created by wind shear and destroyed by buoyancy and dissipation. Since these effects are nearly balanced in the stable ABL, turbulence intensities are usually low and intermittent. In some cases of stagnant stable conditions the horizontal diffusion of the plume can be of the same magnitude or larger than the actual transport. Moreover, turbulent velocities are frequently affected by gravity waves and the stable ABL undergoes non-stationary evolution. Additional dispersion due to wave phenomena also needs to be resolved. During stable conditions the ABL flow usually decouples from the synoptic winds and its flows are dominated by the local circulations. In some cases a low-level jet can develop at the top of the surface stable layer and the fate of pollutants at various elevated layers can be completely different over a very small vertical separation. In contrast, during stable and stagnant conditions the winds close to the surface are weak and sometimes below the detection limit of usual instrumentation. Radiation and advection can also cause fog and cloud formation and significantly change the rate of chemical reactions for some species and deposition processes. The depth of the stable ABL is of the order of 100 m, and radiation processes, as well as local effects such as urban effects, vegetation, soil properties, and small-scale topographic features, can significantly influence ABL characteristics. Plume meandering is frequently observed during stable conditions in topographically complex terrain, and use of data from limited measurement sites can yield erroneous conclusions. All these effects significantly modify transport and dispersion as well as removal of pollutants. Consequently, an extensive measurement network is necessary in order to capture the spatial and temporal structure of the ABL in a mesoscale domain. The success in any type of dispersion calculation will be limited to appropriate capture and input of atmospheric parameters.

One of the diagnostic models recommended for this study is CALMET. Wind fields in CALMET are calculated in a user specified number of vertical levels by taking into account the influence of terrain on the atmospheric flow and applying an inverse weighting scheme. The initial terrain-adjusted domain mean horizontal components of the wind at each grid point are modified to obtain the final interpolated wind components. CALMET can calculate a spatially variable initial guess field using objective analysis of the measurements. Moreover, CALMET allows use of gridded wind fields created by a prognostic atmospheric model, such as the Penn State University Meteorological Model (MM4, MM5), as “initial guess” fields or as substitutes for observations. CALMET has detailed algorithms for the depth of the convective layer as a function of the potential temperature lapse rate in the layer above the mixing depth, the time step, and the temperature discontinuity at the top of the mixed layer. The daytime mechanical mixing depth is determined from the Coriolis parameter, the friction velocity and the Brunt-Vaisala frequency in the stable layer above the mixed layer. The nighttime depth of mechanical mixing is determined from the friction velocity. CALMET uses an upwind-positioned averaging scheme to smooth out the mixing depths through use of determined weighting factors. Since CALMET has detailed algorithms for wind fields and mixing depth, and furthermore allows initialization with the output from the prognostic atmospheric model, it is an optimum tool for obtaining the initial meteorological fields necessary for estimation of transport, dispersion, and chemical transformation of atmospheric pollutants.

Based on the complexity of terrain in southern California, the MM5 model developed by Penn State University and the National Center for Atmospheric Research (NCAR) represents an appropriate tool for resolving dynamics and thermodynamics if used on the scale of 1-2 km horizontal resolution with nesting capabilities. It should include a nonhydrostatic option and full parameterization of physical processes including turbulent transfer. MM5 uses an advanced four-dimensional data assimilation scheme connected to either measurements or synoptic fields. However, uncertainty exists as to the extent to which MM5 can be used to infer turbulence properties in complex terrain. One of the main components in the study is a characterization of the origin and fate of atmospheric pollutants in the SoCAB. The main difficulties are due to complex terrain and a number of significant sources within the basin and its surroundings. The results from wind field modeling will be used as an input for dispersion and chemical modeling of relevant pollutants also for the entire intensive study period. Atmospheric modeling should treat formation and evolution of fog and clouds which are essential determinants for liquid-phase chemistry. The detailed information of the three-dimensional plume structure from different sources for the worst case scenarios (highest ground concentrations at the monitoring of interest) will be obtained by wind field, dispersion, and chemical modeling.

The final task is reconciliation of all source apportionment approaches and evaluation of uncertainties, model assumptions, and differences compared to measurements. The main objectives of this task are:

- Simulate atmospheric processes using MM5 in both fully predictive and data assimilation modes. Since a number of airborne and remote sensing upper-air measurements will be available, it is desirable to place emphasis on the data assimilation mode for the entire field program period. The fully prognostic mode may be desirable for understanding basic characteristics of specific weather episodes with high pollutant concentrations.

- Determine flow patterns in southern California with acceptable horizontal and vertical resolution, using physical parameterization of the main atmospheric processes (radiation, moisture, clouds, and fog).

- Provide detailed information on the vertical wind and temperature structure of the atmospheric boundary layer during the case studies. Determine elevated layers with specific stability and dynamics. The vertical structure is essential for estimates of transport and dispersion of atmospheric pollutants, as well as for determination of the amount of decoupling of local flows from the air aloft.

- Determine properties of land-sea breezes, urban circulations, local flows (slope and drainage), and diurnal variation of thermal stability and shear.

- Determine spatial characteristics of mixing depth for both convective and stable conditions.

- Estimate properties of turbulence transfer and associated vertical fluxes in the boundary layer.

- Conduct sensitivity tests of the input parameters (topographic resolution, model grid, synoptic fields vs. radiosonde network, range and variation of sea/surface temperature, urban effects/roughness, sinks and sources of heat).

- Quantify differences between the predicted and observed wind fields and stability parameters for specific case studies.

The *advantages* in using a prognostic modeling approach are:

- High resolution in horizontal and vertical directions.

- Topography with resolution of 30 seconds embedded within the model structure.

- Detailed prognostic fields of meteorological parameters (wind, temperature, humidity, turbulence, radiation, clouds).

- Physically-based estimate of mixing depth in both convective and stable cases, with full spatial and temporal variability.

- Detailed structure of the small-scale local flows that cannot be resolved through simplified parameterization.

- Detailed vertical structure of meteorological parameters and stability, which is especially important near sources and receptors and along the transport path.

The *disadvantages* in using a prognostic modeling approach are:

- The models are fairly complex and expensive to run. Usually they are limited to certain case studies.

- The models have assumptions in simplification of basic differential equations and numerical techniques and in the parameterizations of physical processes.

- Integration with dispersion models is usually one of the critical problems.

Nevertheless, atmospheric models are useful tools in understanding the structure and evolution of boundary layer dynamics and providing meteorological fields as input for dispersion models.

2.6.2 Air Quality Modeling

After numerous air quality modeling efforts over the last two decades, the ARB has provided technical guidance for photochemical modeling (DaMassa *et al.*, 1992). This guidance includes methods for assessing the performance of a model and criteria for accepting a model.

In the application of a model, parameters such as the size of the modeling domain, the number of vertical levels, and the horizontal grid resolution must be chosen to provide adequate

characterization of the physical setting and the major atmospheric features without incurring excessive computer run times. Selection of episodes is also important for providing physical insight into the reasons behind the observed pollutant species concentrations and spatial patterns for those episodes.

In the evaluation of the model, the quality of the input aerometric data and the emission inventory must also be considered. DaMassa *et al.* (1992) provide guidance in classifying these input databases.

2.6.3 Contribution of Transported Pollutants to Ozone Violations in Downwind Areas

Although past transport studies have documented pollutant transport on specific days, they have not always *quantified* the contribution of transported pollutants to ozone violations in the downwind area. Quantitative estimates of the contribution of transported pollutants to ozone violations in the downwind area can be accomplished by photochemical grid modeling and by advanced data analysis techniques such as "flux planes" measured by aircraft which traverse a vertical plane perpendicular to a suspected transport corridor at different elevations.

In principle, well-performing grid models have the ability to quantify transport contributions. However, many of the interbasin transport problems involve complex flow patterns with strong terrain influences which are difficult and expensive to model. Upper-air meteorological and air quality data in critical transport locations is generally required in order to properly evaluate and use grid models for quantifying transport contributions. In combination with modeling, data analyses can improve the evaluation of modeling results and provide additional quantification of transport contributions.

In order to quantify pollutant transport and to provide data for modeling and data analyses, surface and aloft measurements are needed at locations where transport can occur and at the times when transport is occurring. These monitoring locations include in and near mountain passes, along coastlines, offshore, and at various locations in the downwind air basin. For example, when pollutants are transported from the SoCAB to the SCCAB via the overwater route, measurements are needed along the western shore of the SoCAB as pollutants leave the SoCAB, offshore along the westerly transport route, and along the Ventura and/or Santa Barbara shoreline as the pollutants return onshore in the SCCAB.

Previous studies (e.g., Roberts *et al.,* 1993) have used aircraft measurements to calculate transport across flux planes. Vertical planes, intersecting the profiler sites downwind of and perpendicular to the mountainous SoCAB exits, can be defined and will provide estimates of transport through these passes using surface and aircraft measurements of pollutant concentrations and surface and wind profiler data for volume flux estimations. In addition, flux planes can be used to investigate over-the-mountain transport because Smith and Shair (1983), among others, have shown this to be a possible transport route under certain meteorological conditions. Flux planes for SCOS97 are further discussed in Section 11.6

2.7 SCAQS Scientific Findings Relevant to SCOS97

The 1987 Southern California Air Quality Study (SCAQS) was the largest single air pollution study conducted in southern California, with more than $14 million contributed by 10 government, industry, and trade association sponsors. It has served as a prototype for subsequent large-scale field studies in the United States. This section presents a summary of key scientific findings and the operational and organizational lessons learned from SCAQS.

The SCAQS field program plan and field program have been described by Blumenthal *et al.* (1987), Lawson (1990), and Lawson *et al.* (1995). Prior to the 1987 field study, technical support studies were carried out in Los Angeles in the summers of 1985 and 1986 to evaluate methods for sampling important intermediate and product species to be measured in the 1987 field study.

The 1985 Nitrogen Species Methods Comparison Study (NSMCS) evaluated measurement methods for nitric acid, ammonia, nitrous acid, and particulate nitrate, all important participants in the nitrogen air pollution cycle in Southern California. More than 20 research groups participated in the study, and the results have been published in *Atmospheric Environment* (Lawson, 1988).

The 1986 Carbonaceous Species Methods Comparison Study (CSMCS) was conducted to evaluate analytical and sampling methods for gas- and particle-phase carbonaceous pollutants, including formaldehyde and hydrogen peroxide. Thirty research groups took part in the study, and the results have been published in *Aerosol Science and Technology* (Lawson and Hering 1990). The results from the NSMCS and CSMCS were used to design and develop the SCAQS aerosol and gas sampler (Fitz *et al.*, 1989). The data analysis and modeling results, as of mid-1992, have been published in the proceedings of the SCAQS Data Analysis Conference (Fujita, 1993). The NSMCS, CSMCS, and SCAQS have resulted in more than 300 peer-reviewed publications.

The SCAQS field study consisted of 11 intensive study days during five separate episodes in the summer of 1987 and six intensive study days during three separate episodes in the fall of 1987. The summer study was designed to collect data during high ozone periods. The summer study included upper air measurements at six rawinsonde and two airsonde sites, in addition to aircraft measurements. The fall study consisted of six "B" sites and one "A" site and was designed to study air quality during stagnation conditions conducive to buildup of NO_2 and PM_{10}. The "B" sites were established along two separate pollutant transport routes across the SoCAB. Each of these sites contained the specially designed SCAQS aerosol and gas sampler (Fitz *et al.*, 1989; Chow *et al.*, 1993). Two of the "B" sites were heavily instrumented with numerous research projects — the upwind Long Beach site and the downwind Claremont site — these were also called "A" sites. There were 36 "C" sites, which consisted of the routine monitoring sites operated by the SCAQMD and other groups. The fall study also had aircraft measurements, one airsonde, and five rawinsonde sites.

2.7.1 Emissions

- Nonmethane organic gas (NMOG, or nonmethane hydrocarbons plus oxygenated compounds) composition and NMOG to NO_X ratios were similar throughout the SoCAB. This suggests a common source of emissions (presumably motor vehicles), and continuous injection of fresh emissions. However, the total NMOG concentrations had significant spatial, day-to-day, and seasonal variations due to meteorological factors and the non-uniformity of emission rates.

- The 1987 SCAQS Van Nuys Tunnel study suggested that nonmethane hydrocarbon (NMHC) and CO emissions may be underestimated by about a factor of 2 in EMFAC7E, the California Air Resources Board's motor vehicle emission factor model, version 7E (July 1991). Model estimates of NO_X emissions appeared to be in reasonable agreement with the tunnel measurements. These conclusions are consistent with those of other studies throughout the country.

- Measurements in 1987 of ambient NMOG to NO_X ratios were 2 to 2.5 times higher than estimates from EMFAC7E. Ambient CO to NO_X ratios were ♉1.5 times higher than emission ratios (Fujita *et al.*, 1992). (The agreement between ambient and emission NMOG to NO_X ratios has improved since 1987 because ambient NMHC, and presumably NMOG, concentrations have declined faster than the emission model predicts, and the model has been modified to include previously uninventoried sources of NMOG and CO.)

- There is more unburned gasoline in the atmosphere than estimated by the emission inventory. It is not clear whether tailpipe exhaust, evaporative emissions, or fuel spillage is the source of these uninventoried emissions (Harley *et al.*, 1992; Fujita *et al.*, 1994). Since NMOG compositions in other cities in California and the U.S. are similar to the SoCAB, these conclusions may apply to the rest of the country (Fujita *et al.*, 1995).

- The accuracy of the non-motor vehicle component of the emission inventory could not be evaluated because of the proximity of most monitoring stations to roadways and the lack of marker species to provide unique source signatures.

- Airshed model predictions were in better agreement with ozone measurements when the official on-road motor vehicle ROG emissions were increased by substantial margins. ARB (Wagner and Wheeler, 1992) and SCAQMD (Chico *et al.*, 1992) increased total on-road motor vehicle emissions by a factor of 2.5, and Carnegie Mellon/California Institute Technology (Harley *et al.*, 1993) increased hot exhaust emissions by a factor of 3.

- The relative composition of the NMOG inventory is biased toward overestimation of alkenes and underestimation of aromatic hydrocarbons and higher ($>C_2$) carbonyl compounds. The reactivities of the emission inventory composition profiles are about

10 and 30 percent higher than the ambient composition profiles in summer and winter, respectively.

2.1.2 Factors Controlling Ozone Accumulation

- Nitrous acid (HONO), directly emitted and presumably formed by nighttime reactions involving NO_X, water, and aerosols, is potentially the single largest source of hydroxyl radicals that initiate the ozone photochemistry in the early part of the day.

- There appears to be a large amount of carbonyl species formation in the urban atmosphere from photo-oxidation of hydrocarbons. The secondary photochemical contributions to C_1 to C_4 carbonyl compounds are probably larger than the primary source contributions, although the peak concentration events are dominated by primary source contributions. Sources of C_{4+} carbonyl compounds could not be identified. Some evidence indicates landfills, and perhaps microbial decomposition of industrial, household, and agricultural waste products, as primary sources of C_{4+} carbonyl compounds.

- Overall, biogenic hydrocarbons play a small role in ozone formation in the urban area of the SoCAB. On average, isoprene contributed 0.2 percent of the NMOG carbon, and 0.7 percent of the NMOG reactivity (using the maximum incremental reactivity scale of Carter *et al.*, 1994) in the summer. However, because isoprene reacts rapidly, and because the measurement system did not measure the intermediate products of isoprene reactions, the ambient measurements underestimate its relative contribution.

- Although the hydrocarbon measurement system was set up to detect monoterpenes, none were found.

2.1.3 Performance of Urban-Scale Models

- The airshed models used to model the SCAQS episodes appear to underpredict NO_X oxidation products, leading to concerns about their ability to quantify the effectiveness of NO_X controls.

- High concentrations of ozone and other pollutants were often found aloft in layers covering much of the SoCAB near the top of the daytime mixed layer. Model predictions of ozone aloft for one of the case studies were about 0.05 to over 0.10 ppm less than the measured concentrations. In the surface layer, depending on the model application and location in the modeling domain, predicted ozone concentrations were significantly lower or higher than observations.

- Because current airshed modeling efforts may be missing an important upper air recirculation feature, uncertainties in the modeling results must be determined and potentially reduced. Models should not use a terrain-following coordinate system, as the observed pollutant and temperature structure aloft appears to be more horizontal

in nature. Clean boundary conditions should be used above the mixed layer, typically above 1,500 to 2,000 meters.

2.1.4 Management of Ozone Accumulation

- Under the combined NMOG and NO_X control program in the SoCAB, peak ozone concentrations have declined by 20 percent and exposure to unhealthful concentrations has declined by 50 percent since the early 1980s; at the same time, concentrations of NMOG have declined by about 40 percent and concentrations of both NO_X and CO have declined by about 20 percent.

- Consensus exists that NMOG and CO emissions from motor vehicles are significantly underestimated, but there is no agreement on the cause.

- Further refinement of models applied in the SoCAB is needed, as the current treatment of recirculation, and possible underestimation of ROG emission rates may underestimate the benefits of NO_X control strategies.

- Modeling studies for a range of ozone episodes and base emission inventories determined that the maximum incremental reactivity (MIR) scale is a valid approach for reactivity scaling of NMOG emissions (National Research Council, 1991).

2.1.5 Potential Nationwide Research Needs Arising from SCAQS

- Top-down comparisons of ambient measurements with the emission inventories have demonstrated a need for more accurate methods of assessing the contribution and importance of various pollution source types on air quality in urban areas.

- Conditions aloft have a significant influence on surface air quality; boundary conditions also have a significant influence on modeling results. Development of reliable and cost-effective methods for measuring meteorological conditions and pollutant concentrations (aloft and in "clean" air) is needed to support modeling applications.

- Smog formation is sensitive to small concentrations of critical pollutants such as hydroxyl and hydroperoxy radicals, nitrous acid, etc. Development of reliable methods for measuring these critical compounds is needed to support modeling applications.

- The performance of photochemical models is somewhat dependent on their formulation. Improvements are needed in the meteorological and chemical formulations to improve model accuracy, precision, and validity.